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XRAM Acc No: C87-083691
XRPX Acc No: N87-149786
Photosensitive resin compsn. for positive-type resist - contains alkali-soluble organosilicon polymer and orthoquinonediazide cpd. and is resistant to oxygen plasma
Patent Assignee: HITACHI LTD (HITA)
Inventor: INOUE T; MIZUSHIMA A; NATE K
Number of Countries: 004 Number of Patents: 005
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Main IPC	Week
EP 229629	A	19870722	EP 87100100	A	19870107		198729 B
JP 62159141	A	19870715	JP 86501	A	19860108		198734
EP 229629	B	19910320					199112
DE 3768663	G	19910425					199118
JP 2619358	B2	19970611	JP 86501	A	19860108	G03F-007/075	199728

Priority Applications (No Type Date): JP 86501 A 19860108
Language, Pages: EP 229629 (E, 43); JP 2619358 (12)
Abstract (Basic): EP 229629 A
A photosensitive resin compsn. comprises an alkali-soluble organometallic polymer (I) and a photosensitive dissolution inhibitor (II) as the major constituents. (I) is a polymer in which all or a pt. of the metallic element is present in the main chain, and all or pt. of the side chains are organic gps. having phenolic hydroxyl gps..

(I) are used as polymers contg. at least one of Si, Ge, Sn and Ti, esp. pref. are alkali-soluble organosilicon polymers selected from; (i) silmethyl polymers contg. more than 40%, in the polymer skeleton, of units of formula (a), or (ii) siloxane polymer contg. more than 40%, in the skeleton, of units of formula (b), or (iii) polyorganosilsesquioxane polymer contg. more than 40%, in the skeleton, of units of formula (R7-SiO3/2), in which at least one of the side chains in each polymer = an organic gp. having a phenolic hydroxyl gp., R1-7 = monovalent organic gps., pref. R1 and R2 = methyl, R3 = H, R4 = p-hydroxyphenyl, R5 = methyl, R6 = p-hydroxybenzyl and R7 = p-hydroxybenzyl; and (II) as an o-quinonediazide, pref. a 1,2-naphthoquinoneazide of formula (III) (where R8 = monovalent organic gp.).

USE/ADVANTAGE - The compsn. is suitable for use as the top layer resist used in the two-layer resist process. It is used as a positive type resist which can be developed with an alkali developing soln., and has high sensitivity, high resolution and resistance to oxygen plasma. It is esp. used to form fine patterns on a silicon wafer for the production of semiconductor elements.

0/0
Abstract (Equivalent): EP 229629 B
A photosensitive resin compsn. comprises an alkali-soluble organometallic polymer (I) and a photosensitive dissolution inhibitor (II) as the major constituents. (I) is a polymer in which all or a pt. of the metallic element is present in the main chain, and all or pt. of the side chains are organic gps. having phenolic hydroxyl gps..

(I) are used as polymers contg. at least one of Si, Ge, Sn and Ti, esp. pref. are alkali-soluble organosilicon polymers selected from; (i) silmethyl polymers contg. more than 40%, in the polymer skeleton, of units of formula (a), or (ii) siloxane polymer contg. more than 40%, in the skeleton, of units of formula (b), or (iii) polyorganosilsesquioxane polymer contg. more than 40%, in the skeleton, of units of formula (R7-SiO3/2), in which at least one of the side chains in each polymer = an organic gp. having a phenolic hydroxyl gp., R1-7 = monovalent organic gps., pref. R1 and R2 = methyl, R3 = H, R4 = p-hydroxyphenyl, R5 = methyl, R6 = p-hydroxybenzyl and R7 = p-hydroxybenzyl; and (II) as an o-quinonediazide, pref. a

1,2-naphthoquinoneazide of formula (III) (where R8 = monovalent organic gp.).

USE/ADVANTAGE - The compsn. is suitable for use as the top layer resist used in the two-layer resist process. It is used as a positive type resist which can be developed with an alkali developing soln., and has high sensitivity, high resolution and resistance to oxygen plasma. It is esp. used to form fine patterns on a silicon wafer for the production of semiconductor elements. (43pp Dwg.No.0/0)

Polysiloxane-composite polymer particles

Patent number: EP0449263

Publication date: 1991-10-02

Inventor: NAKAMURA KATSUHIRO (JP); KATO MINORU (JP); WATANABE YASUHISA (JP); MATSUBARA YASUNORI (JP); IKEDA YORINOBU (JP); YONEKAWA YOSHIAKI (JP); MIKI HIROYUKI (JP); HIRAHARU AKIO (JP); ITO NOBUYUKI (JP); KURITA OSAMU (JP); KANEKO YASUNOBU (JP); NISHIDA SHOUZOU (JP)

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Classification:

- international: C08G77/06; C08J3/03; C08L9/00; C08L25/02; C08L33/00; C08L83/04; C09D133/06; C09D183/04

- european: C08G77/06; C08L83/04; C09D7/12M; C09G1/16

Application number: EP19910104895 19910327

Priority number(s): JP19900079698 19900328; JP19900171024 19900628

Also published as:

EP0449263 (A3)
EP0449263 (B1)

Cited documents:

FR2166085
EP0340580
WO9008810

Abstract of **EP0449263**

Polymer particles in which polysiloxane is composed is disclosed. The polymer particles are prepared by condensing at least one organosilane compound in the presence of organic polymer particles which are prepared from specific monomers and dispersed in an aqueous medium. The polymer particles possess excellent water resistance, weatherability, water repellency, adhesion, and flexing resistance, and thus are useful as water paints, coating agents, carpet packing material, floor polishing agents, cementing medium, and the like.

Hermetic substrate coatings in an inert gas atmosphere

Patent number:	EP0427395
Publication date:	1991-05-15
Inventor:	HALUSKA LOREN ANDREW (US)
Applicant:	DOW CORNING (US)
Classification:	
- international:	H01L21/56; H01L23/29
- european:	C09D183/04; H01L21/56; H01L23/29C
Application number:	EP19900311008 19901008
Priority number(s):	US19890423317 19891018

Also published as:

JP3183675 (A)
EP0427395 (B1)

Cited documents:

EP0270229
EP0270241
EP0226208

Abstract of **EP0427395**

The present invention relates to a method of forming a ceramic or ceramic-like coating on a substrate in the absence of oxygen. The method comprises coating the substrate with a solution comprising a solvent and one or more preceramic materials selected from the group consisting of hydrogen silsesquioxane and hydrolyzed or partially hydrolyzed RxSi(OR)4-x wherein R is independently selected from the group consisting of alkyl, aryl and unsaturated hydrocarbons and x is 0-2. The solvent is evaporated and a preceramic coating thereby deposited on the substrate. The preceramic coating is then ceramified by heating the coated substrate to a temperature of between about 500 up to about 1000 DEG C. under an inert gas atmosphere to thereby produce a ceramic or ceramic-like coating on the substrate. The process of the invention is useful for forming protective coatings on any substrate prone to oxidation at the temperature necessary for ceramification. The present invention also relates to the formation of additional ceramic coatings on the ceramic or ceramic-like coating formed above.

Multilayer ceramic coatings from metal oxides and hydrogen silsequioxane resin ceramified in ammonia

Patent number: EP0323186
Publication date: 1989-07-05
Inventor: HALUSKA LOREN ANDREW; MICHAEL KEITH WINTON; TARHAY LEO
Applicant: DOW CORNING (US)
Classification:
- international: C04B41/52; H01L21/314; H01L21/56
- european: H01L21/314; H01L21/314B1; H01L21/56
Application number: EP19880312293 19881223
Priority number(s): US19870138744 19871228

Also published as:

US4849296 (A1)
JP1204432 (A)
EP0323186 (A3)
EP0323186 (B1)

Cited documents:

EP0270263
US3615272

Abstract of **EP0323186**

Mixtures of hydrogen silsesquioxane resin and metal oxide precursors such as acyloxy and alkoxy compounds of aluminum, zirconium and titanium can be coated on substrates and subsequently ceramified at low temperature in the presence of ammonia, with or without platinum or rhodium catalysis, to form a nitrided ceramic coating on the surface of the substrate. The nitrided coatings produced are useful as interlevel dielectric films or for planarizing and protecting the surface of electronic devices. For further surface protection, overcoating the nitrided coating with an additional layer of a passivating ceramic material and a top layer of a barrier ceramic material is also described.

Use of Alkali-Soluble Polyorganosilsesquioxane Polymers in a resist for preparing electronics parts

Patent number: EP0204963

Publication date: 1986-12-17

Inventor: SUGIYAMA HISASHI; NATE KAZUO; INOUE TAKASHI; MIZUSHIMA AKIKO

Applicant: HITACHI LTD (JP)

Classification:

- **international:** C08G77/14; C08G77/60; G03F7/10
- **european:** C08G77/14; C08G77/60; G03F7/075M

Application number: EP19860106238 19860507

Priority number(s): JP19860000510 19860108; JP19850098032 19850510; JP19850182950 19850822; JP19850236344 19851024

Also published as:

EP0204963 (A3)
EP0204963 (B1)

Cited documents:

GB1022742
US3579467
EP0147127
GB1203071
EP0049127
more >>

Abstract of **EP0204963**

There are provided an alkali-soluble siloxane polymer, an alkali-soluble silmethylene polymer, and an alkali-soluble polyorganosilsesquioxane polymer. They are useful as a photoresist for the fabrication of semiconductor devices. They are suitable for dry etching because of their superior resistance to oxygen plasmas.

Near UV photoresist

Patent number: EP0423446
Publication date: 1991-04-24
Inventor: LAMOLA ANGELO A (US); CALABRESE GARY (US); SINTA ROGER (US)
Applicant: SHIPLEY CO (US)
Classification:
- international: G03F7/038
- european: G03F7/004D; G03F7/038
Application number: EP19900114949 19900803
Priority number(s): US19890422621 19891017

Also published as:

JP3144650 (A)
EP0423446 (B1)

Cited documents:

US4442197
FR1579538
US3595664
US3169868

Abstract of **EP0423446**

A photoacid-generating photoresist composition sensitized with an aromatic, multi-ring, heterocyclic nitrogen containing sensitizer, preferably a ring extended phenothiazine derivative. The use of the sensitizer permits exposure of photoresists to near UV irradiation where such photoresists have heretofore been exposed to deep UV irradiation. The invention is especially useful for acid hardening photoresist systems.

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L2: Entry 1 of 2 File: JPAB Mar 1, 1994

PUB-NO: JP406056560A
DOCUMENT-IDENTIFIER: JP 06056560 A
TITLE: SOG COMPOSITION AND PRODUCTION OF SEMICONDUCTOR DEVICE BY USING THIS COMPOSITION

PUBN-DATE: March 1, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
TANAKA, YASUSHI	

ASSIGNEE-INFORMATION:

NAME	COUNTRY
SONY CORP	

APPL-NO: JP04211898
APPL-DATE: August 10, 1992

INT-CL (IPC): C04B 41/85; H01L 21/316

ABSTRACT:

PURPOSE: To decrease variations of line widths by applying specific SOG on a semiconductor substrate and applying a photoresist thereon, then exposing and developing this photoresist to form resist patterns and executing dry etching.

CONSTITUTION: An SOG compsn. is prepd. by dissolving a silicon compd. in an org. solvent, etc., then mixing a glassy material forming agent, org. binder, etc., with the soln. to prepare an SOG base, then compounding ≥1 kinds of dyestuff among benzoanthracene, 9-methyl anthracene and curimine, etc., absorbing exposing light of 240 to 450nm wavelength with this base. An insulating film 12 is then formed on an Si substrate 11 and wirings 13 are patterned thereon. After an SiO2 film 14 is deposited over the entire surface, the SOG compsn. is applied thereon and is heat treated to form a cured SOG film 15. Further, an SiO2 film 16 is deposited thereon and a resist is applied thereon. The formed resist film 17 is exposed to open contact holes. The resist patterns 17A are developed and with these patterns as a mask, the dry etching is executed, by which the semiconductor device is obtd.

Japan Patent Office
Kokai Patent Publication No. 50645 – 1980, April 12, 1980

Semiconductor apparatus

Patent Application No. 122596 – 1978
Date of Application: October 6, 1978

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Attorney: T. Usuda, Patent Counsel

Continued to the last page

Specification

1. Title of Invention: Semiconductor apparatus

2. Claims of the Patent

Semiconductor apparatus which is characterized by that, in the semiconductor apparatus prepared by gluing and sealing the surface of semiconductor element with a resin, the semiconductor surface and the resin of its vicinity are composed of the crosslinking, ladder type, organo silicone polymer.

3. Detailed Description of the Invention

This invention is related to the surface stabilization of semiconductor surface.

In the past, to stabilize the surface of semiconductor element such as the diode, transistor, integrated circuit, etc., the film of silicon dioxide, silicon nitride, alumina, phosphorus glass, poly imide resin, etc. was formed on the semiconductor substrate that has the semiconductor elements.

In these film materials, there were the following problems, respectively.

(1) When the inorganic compound such as silicon dioxide, silicon nitride, alumina, phosphorus glass is vapor- deposited from vapor phase, the semiconductor element is exposed to a high temperature of 700 ~ 900 deg C. At such a high temperature, the semiconductor element experiences the fluctuation of the recombination velocity of carrier and surface state density and the increase of crystalline lattice defect and so the degradation of element characteristics occurs.

(2) When the said inorganic compound is used as the insulating material on the substrate which has the semiconductor element and the multi-layered wiring structure is formed by using aluminum, etc. as the conductor, level differences are generated on the substrate surface depending on the insulator, the conductor part or the upper and lower connection parts and so the high layer wiring and the refining of wiring become difficult.

(3) In order to solve these problems, the method of applying the heat- resistant organic compound such as poly imide resin varnish in place of said inorganic substances by using a spinner and heat- hardening this at a temperature of 250 ~ 350 deg C has been used. When this method is used, overheating of the element can be prevented and, furthermore, the differences of surface level generated at the wiring conductor or at the upper and lower connecting parts are smoothened by the insulating material and so there is the advantage that the multi- layer wiring can be formed easily. However, the poly imide resin absorbs moisture easily and the moisture absorption causes the dielectric constant, dielectric loss tangent, volume resistivity and the decrease of adhesion and so there was the problem that, by this, the degradation of element characteristics and the corrosion and breaking of conductor occurred.

Objective of this invention is to provide a new semiconductor apparatus from which the above described shortcomings of the existing semiconductor apparatus were eliminated.

This invention is characterized by that the surface- stabilized film that did not exist in the past technology is formed by using the crosslinking, ladder type, organo silicone polymer on the semiconductor substrate.

The crosslinking, ladder type organo silicone polymer has the structure of the following general formula.

(1)

where 1 , m are integers and R_1 is a group having a relatively high heat resistance, such as phenyl group, methyl group, etc. As for R_2, there is no particular restriction as long as it can form a crosslinking bond between the ladder type organo silicone polymers. Examples of R_2 are the following groups.

(2)

(a) Alkyl group; (b) Hydroxy alkyl group; (c) Mercapto alkyl group; (d) Halogenated alkyl group; (e) Aminated alkyl group; (f) Alkylated phenyl group; (g) Halogenated phenyl group; (h) Aminated phenyl group; (i) Vinyl group

In the crosslinking, ladder type organo silicone polymer, the range of R2 / (R1 + R2) (mol ratio) gives the desirable physical properties. When the R2 / (R1 + R2) exceeds 0.2, mechanical strength of the crosslinked material drops and when the R2 / (R1 + R2) goes below 0.005, the solvent resistance drops.

The crosslinking, ladder type, silicone polymer is soluble in the solvent such as benzene, N- methyl –2- pyrolidone, 1, 1, 1 – trichloro ethane, o- dichloro benzene, tetralin, cyclo hexanone, veratrole, etc.

For the formation of coating film, the drying of solvent and the crosslinking reaction are conducted at the temperature of 100 ~ 350 deg C after applying the said ladder type organo silicone polymer by using a spinner on the semiconductor substrate at a temperature near the room temperature.

Also, the processing of the crosslinking, ladder type organo silicone polymer film is conducted with the film for which the solvent drying was conducted at a relatively low temperature where the crosslinking reaction does not occur, by using the method of solvent etching with photo resist and the method of plasma etching with the photo resist to the film material for which the crosslinking reaction was let to occur.

The crosslinking bond that is obtained by heating the said ladder type organo silicone polymer depends on the type of R2 and so it is not fixed. But, for example, it is believed to be the bond of the following type.

(3)

Even without the crosslinking, the crosslinking, ladder type organo silicone polymer can be used in the surface stabilization of semiconductor element but, as the semi conductor element is exposed to many types of acid, alkali and organic solvents in the wiring forming process and washing process, the crosslinking is important for the purpose of improving the stability of coating film against these chemicals.

When, for example, a phenyl group is used for R_1 in the crosslinked ladder type organo silicone polymer, the polymer has enough heat resistance to resist decomposition up to 450 ~ 500 deg C and it can thermally endure the heat treatment that is given during the production process such as that of the integrated circuit and, also, it can endure the reliability test in a high temperature atmosphere (200 ~ 300 deg C) which is conducted commonly.

The crosslinked ladder type organo silicone polymer has excellent adhesion to the semiconductor elements and metallic materials and, furthermore, this does not drop even when it is kept at a high temperature.

Dielectric constant of the crosslinked ladder type organo silicone polymer is less than 3 and so it is lower in comparison to 3.8 of silicon dioxide, 6.5 of silicon nitride and 9.0 of alumina and, furthermore, it has the insulation property of high level. Therefore, it is possible to make the element which has higher level of insulation characteristics than the existing semiconductor elements.

In the following, the invention is explained by using examples of application.

Example of Application 1

98 mol % of phenyl triethoxy silane and 2 mol % of γ- phenyl amino propyl triethoxy silane were heat- polymerized by using KOH catalyst in diphenyl to obtain the crosslinking ladder type organo silicone polymer. The viscosity ratio of the 1 wt % benzene solution of this polymer and the benzene at 25 deg C was 1.7.

As shown in Fig. 1 (A), the base zone 2 and the emitter zone 3 were formed by the impurity diffusion process on the silicone substrate 1 which serves as the collector zone also. On the surface of this, the cyclo hexanone solution of the said polymer was applied by using a spinner and this was heated for 1 hour at 150 deg C to conduct the drying of solvent, to obtain the polymer coating film 4 as shown in Fig. 1 (B). Next, at the upper side of the electrode lead-out openings of the collector zone, base zone and emitter zone, there was formed the photo resist layer 5 with the window openings as shown in Fig. 1 (C).

After this, the said polymer coating film was etched by using 1, 1, 1 – trichloro ethane to remove the photo resist layer to form the electrode lead-out openings as shown in Fig.1 (D) and, in continuation, a heat treatment at 350 deg C for 1 hour was conducted to have the crosslinked ladder type silicone polymer coating film. Further, as shown in Fig. 1 (E), (F), vapor deposition of aluminum 6, formation of the photo resist 7 and etching and eli-

mination of photo resist were conducted to form the collector electrode 8, collector electrode 9 and emitter electrode 10.

In the transistor which was formed as described above, in comparison to the transistor of the same shape where the phosphorus glass was used, the leak current in the reverse direction between the collector – base decreased by 15 %.

Example of Application 2

95 mol % of phenyl triethoxy silane and γ- amino propyl triethoxy silane were heat-polymerized by using KOH catalyst in diphenyl to obtain the crosslinking ladder type organo silicone polymer. Viscosity ratio of the 1 % benzene solution of this polymer and the benzene at 20 deg C was 1.5.

The cyclo hexanone solution of this polymer was applied on the common MOS type transistor by using a spinner and this was heated at 350 deg C for 1 hour to conduct the drying of the solvent and the crosslinking reaction to form the cross linked ladder type silicone polymer coating film of film thickness 2 μ. This coating film did not dissolve even when it was given ultra sonic washing for 5 minutes in 1, 1, 1 – tri chloro ethane. With the MOS type transistor obtained in this way, the leak current between the source drain electrodes was stabilized even after 10,000 hours of mounted test at 170 deg C.

Also, when the similar elements were subjected to 10,000 hours of mounted test at a high temperature high humidity of 85 deg C and 85 % RH, the ratio of defect was less than 1 %.

With the MOS type transistor treated with poly imide resin obtained by the similar method, the leak current was stable in the 170 deg C 10,000 hour mounted test but, in the mounted test at 80 deg C 85 % RH, the defect ratio reached 20 %.

Example of Application 3

94 mol % of phenyl triethoxy silane and 6 mol % of tolyl triethoxy silane were heat-polymerized by using KOH catalyst in diphenyl to obtain the crosslinking ladder type organo silicone polymer.

The viscosity ratio of the 1 % benzene solution of this polymer and the benzene at 25 deg C was 2.0.

Fig. 2 (A), (B) are the semiconductor apparatus made by sealing the semiconductor integrated circuit 11 with the molding resin 12. The bonding pad 13 and the external connection lead 14 are connected by the thin metallic wire 15. The said polymer solution was dropped to cover this integrated circuit 11, thin metallic wire 15 and the external connection lead 14 and heating was conducted at 350 deg C for 3 hours to form the crosslinked ladder type organo silicone coating film 16 and, further, its outer side was sealed with the molding resin. This apparatus was given a trial operating test in an

atmosphere of 85 deg C and 85 % RH. Compared to the case of using the poly imide resin, a life time of about 2 times was exhibited.

Example of Application 4

95 mol % of methyl triethoxy silane and 5 mol % of γ- amino propyl triethoxy silane were heat- polymerized by using KOH catalyst in diphenyl to obtain the crosslinking ladder type organo silicone polymer. The viscosity ratio of the 1 % benzene solution of this polymer and the benzene at 25 deg C was 1.4.

On the thin film circuit that was formed on the alumina substrate, the semiconductor integrated circuit was mounted and the cyclo hexanone solution of the said polymer was dropped to cover the connection part of the semiconductor surface and the thin film circuit and a heat treatment at 300 deg C for 2 hour was done to conducted the drying of solvent and the crosslinking reaction. This polymer film was stable even after the circuit was soldered and the whole circuit was washed with 1, 1, 1 – trichloro ethane.

To this circuit, resin molding was applied and the pressurized water penetration was conducted and a durability of the one for which the said polymer was used was found to be 2 times or more relative to the one for which poly imide resin was used.

When this invention is used, as has been described, stabilization of the semiconductor surface can be conducted easily by the polymer coating film having excellent heat resistance, moisture resistance, solvent resistance, electrical properties and adhesion and, by this, the semiconductor apparatus of high reliability can be obtained.

4. Brief Description of the Figures

Fig. 1 (A) ~ (F) show the process of installing the electrodes at the surface- stabilized film prepared by the crosslinking ladder type organo silicone polymer and to the element on the semiconductor substrate that has the transistor. Fig. 2 (A) shows the major cross section diagram of the semiconductor integrated circuit apparatus. Fig. 2 (B) is the top view of the cut-open main part of the semiconductor integrated circuit apparatus.

1: Silicon substrate; 2: Base zone; 3: Emitter zone; 4: Polymer coating film; 5, 7: Photo resist; 6: Aluminum vapor deposited film; 8, 9, 10: Aluminum electrodes; 11: Semiconductor integrated circuit; 12: Molding resin; 13: Bonding pad; 13: External connection lead; 15: Metallic wire; 16: Polymer coating film

Attorney: T. Usuda, Patent Counsel

Fig. 1

Fig. 2

Continuation from P. 1.

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